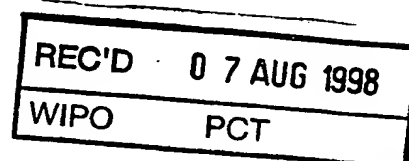




PCT/AU98/00576



09/463423
**PRIORITY
DOCUMENT**

Patent Office
Canberra

SUBMITTED OR TRANSMITTED IN
COMPLIANCE WITH RULE 17.1(a) OR (b)

I, KIM MARSHALL, MANAGER EXAMINATION SUPPORT AND SALES,
hereby certify that the annexed is a true copy of the Provisional specification in
connection with Application No. PO 8196 for a patent by AUSTRALIAN
NUCLEAR SCIENCE AND TECHNOLOGY ORGANISATION and CRC FOR
WASTE MANAGEMENT AND POLLUTION CONTROL LIMITED filed on
23 July 1997.

I further certify that the annexed specification is not, as yet, open to public inspection.



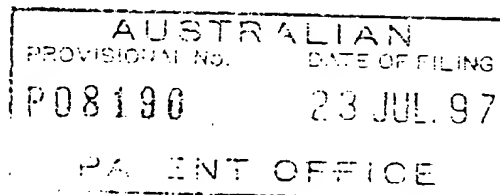
WITNESS my hand this Twenty-Eighth
day of July 1998

KIM MARSHALL
MANAGER EXAMINATION SUPPORT AND
SALES

AUSTRALIA
Patents Act 1990

PROVISIONAL SPECIFICATION

Invention Title: Photo-Assisted Oxidation of Inorganic Species in
 Aqueous Solutions



The invention is described in the following statement:

GH REF: P25013-A/RPW:SLC

PHOTO-ASSISTED OXIDATION OF INORGANIC SPECIES
IN AQUEOUS SOLUTIONS

Field of the Invention

5 The present invention relates to a method for oxidising
inorganic species in aqueous solutions, and more
particularly, to the treating of contaminants in e.g. human
drinking water, and industrial waste waters and process
liquors. However, it should be appreciated that the
10 invention can be employed wherever it is necessary to
oxidise an inorganic species for whatever reason.

Background to the Invention

 Dissolved sulphur dioxide or sulphite is usually
considered to be a reducing agent. Further, it is known
15 that the oxidation of sulphite is accelerated through
exposure to UV radiation (Matthews, J.H. et.al.
J.Am.Chem.Soc.1917,39, 635). Matthews teaches, however,
that oxidation is retarded by the presence of trace amounts
of various species. In addition, no change in the oxidation
20 state of these species was observed.

 Many drinking water supplies across the world are
contaminated by trace contaminants such as arsenic, cyanide,
manganese, sulphide and selenium. World Health
Organisation standards require very low levels of
25 contaminants (for example arsenic-a 10 ppb limit, selenium-a
10ppb limit). The presence of manganese gives rise to
"dirty water" problems and can result in soiling of clothes
and staining of household fixtures when present in
concentrations in excess of 20 ppb in drinking water.

30 Many waste waters and mineral processing liquors from
industry also include cyanide, arsenic, iron, manganese,
selenium, and in the field of nuclear technology, uranium.

 As part of the removal process, chemical oxidants such
as chlorine, ozone and permanganate are often used.
35 However, these oxidants can give rise to harmful byproducts
such as chloroform, and the presence of residual

permanganate can produce discoloured waters.

Summary of the Invention

The present invention provides a method for oxidising an inorganic species in an aqueous solution comprising the steps of:

(i) supplying an oxidisable source of sulphur, and oxygen to the solution; and

(ii) irradiating the solution with UV light such that the species is oxidised.

In the present invention, oxygen is advantageously used as the oxidising agent, with no residual contaminating after-effects. Sulphur sources can be selected, (e.g. sulphite) such that in the oxidising procedure, a relatively benign product is produced (e.g. sulphate).

The oxidisable sources of sulphur can be SO_3^{2-} , S^{2-} , HS^- , $\text{SO}_2(\text{g})$, aqueous SO_2 , or HSO_3^- . However, sulphur dioxide and sulphite are the most preferred sources.

Typically the process is applied in the treatment of trace quantities of inorganic species but the process can also find application with more concentrated quantities of contaminants.

Typically the species oxidised include one or more of arsenic, cyanide, manganese, sulphide, selenium, vanadium, cerium, nickel, uranium or iron.

Typically the ultraviolet light employed has a wavelength of about 254nm. Radiation can be supplied continuously or in pulses. Furthermore, low, medium or high pressure mercury arc lamps can be used as the source of the UV radiation. Alternatively, sunlight or UV radiation from a laser source can be employed.

Typically the oxygen is sparged into the aqueous solution as air but other methods of addition are possible. As indicated above, the solution is typically a drinking water solution, an industrial waste water or process liquor etc.

Typically the pH of the solution is, if necessary, made

to be approximately neutral or basic.

Brief Description of the Drawings

Notwithstanding any other forms which may fall within the scope of the present invention, preferred forms of the invention will now be described, by way of example only, with reference to the accompanying drawings and the following non-limiting examples. In the drawings:

Figure 1 is a graph that plots the increase in the concentration of arsenic (V), during the oxidation of arsenic (III) to arsenic (V), using a preferred process according to the present invention; and

Figure 2 is a graph showing the effect on arsenic oxidation of varying concentrations of sulphite.

Modes for Carrying Out the Invention

Preferred forms of the present invention find application in the treatment of drinking water, waste waters and mineral processing liquors. It should be appreciated, however, that the invention has broader applications.

With drinking water treatment, it is desirable to remove trace oxidisable contaminants, such as arsenic, cyanide, manganese, sulphide and selenium. In at least preferred forms, contaminants are oxidised and then removed under neutral or slightly alkaline conditions.

In the treatment of waste waters and mineral processing liquors, it is desirable to neutralise and/or remove (depending on the final use of the water or liquor) species such as cyanide, arsenic, iron, manganese and selenium. In these applications, however, oxidation may take place in acid, neutral or alkaline conditions.

Manganese-related "dirty water" problems are a significant water quality issue to water supply authorities. It is understood that 40 per cent of public water supplies in the United States have manganese concentrations exceeding levels of 10-20ppb.

Manganese is also a problem in processed wastes in the milling of uranium ores. Manganese is often present in the

ore to be milled, and may be also introduced as an oxidant in the form of a pyrolusite (MnO_2) which is an oxidant used in the leaching of uranium.

5 Dissolved cyanide in waste waters must be removed for environmental reasons. In industrial process liquors, it is necessary to oxidise various metal ions as part of the overall processing in the plant.

Details of various preferred process operating parameters are now described.

10 Source of Radiant Energy

Any source of radiant energy in the UV region of the electromagnetic spectrum was observed to be useful, provided that the radiation was absorbed by the dissolved sulphur compound which was acting as the photo-initiator
15 of the process. Low pressure mercury arc lamps were used for the oxidation of dissolved arsenic (III) and manganese(II). Typical UV wavelengths of less than 300nm were employed (preferably about 254nm).

Choice of Photo-Absorber

20 Dissolved sulphur species absorbed the supplied UV light and were oxidised by dissolved oxygen. These sulphur species were used up (oxidised) during the photochemical reaction. Dissolved sulphur(IV) derived from sodium sulphite and dissolved sulphide from sodium
25 sulphide were used for the oxidation of arsenic(III). Dissolved sulphite from sodium sulphite was used for the oxidation of manganese(II).

Furthermore, dissolved sulphite was obtained by sparging sulphur dioxide gas or a gas mixture of sulphur
30 dioxide and air/oxygen/nitrogen into the solution. Thiosulphate or tetrathionate compounds were used as an alternative sulphite source. Thus, the forms of sulphur employable included SO_3^{2-} , $\text{SO}_2(\text{g})$, aqueous SO_2 , S^{2-} , HS^- and HSO_3^- , $\text{S}_2\text{O}_3^{2-}$, $\text{S}_4\text{O}_6^{2-}$.

35 Source of Oxidant

Oxygen was the oxidant for the photochemical

oxidation process. It was typically supplied at about 0.2 atmospheres partial pressure by aerating the reaction mixture. Alternatively, oxygen was supplied by sparging a gas mixture of sulphur dioxide with air, or an oxygen/nitrogen mixture into the solution (or any other compatible gas source). Oxygen partial pressures greater than or less than 0.2 atm can also be used as appropriate.

It was noted that where the UV source chosen emitted light at a wavelength at about or below 190 nm, ozone was generated from the dissolved oxygen; (ozone is a powerful oxidant which can oxidise arsenic(III) and manganese(II)). For the examples described below, non-ozone producing lamps were employed.

Examples

Further non-limiting examples will now be described.

Photo-Oxidation of Dissolved Arsenic(III)

A reaction mixture (1700 mL) containing 470 µg/L As(III) (typical concentrations in ground water in areas where arsenic is leached from the naturally occurring arsenic-containing minerals) and 10 mg/L of dissolved sulphite (SO_3^{2-}) was prepared as follows: the sulphite stock solution was prepared by dissolving sodium sulphite salt in demineralised water; the arsenious acid (As(III)) solution was obtained by dissolving arsenic trioxide in warm, demineralised water. The pH of the reaction mixture was adjusted to 9 with the addition of sodium carbonate (because groundwaters typically have significant carbonate alkalinity). The solution was then aerated by the injection of fine bubbles of air.

In the absence of UV illumination, no significant oxidation of As(III) was observed (Figure 1). When a 15 W low pressure mercury lamp was switched on to illuminate the reaction mixture, the oxidation of As(III) and S(IV) proceeded rapidly (Figure 1).

The experiments were repeated using various initial concentrations of dissolved sulphite, namely from 0 to 12

mg/L of dissolved sulphite. As shown in Figure 2, the rate of As(III) oxidation was strongly dependent on the initial sulphite concentration when it was less than 8 mg/L. Figures 1 and 2 demonstrate that both UV light and dissolved sulphite were needed for the photo-oxidation reaction to occur.

Actinometry determination using potassium ferrioxalate showed that a maximum of 6 Watts of 254 nm radiation produced by the 15 W lamp was absorbed by the reaction mixture. Total As and As(III) concentrations were determined using atomic absorption spectroscopy with hydride generation. Concentrations of As(V) in the reaction mixture were determined using the molybdenum blue spectrophotometric method (Johnson D. and Pilson M., Analytical Chimica Acta, 58, 289-299 (1972)). Sulphite concentrations were also determined spectrophotometrically (Humphrey R.E., Ward M.H. and Hinze W., Analytical Chemistry, 42, 698-702 (1970)).

Photo-Oxidation of Dissolved Manganese(II)

A reaction mixture (1700 mL) containing 500 µg/L Mn(II) (typical concentrations in surface and ground water are less than 1 mg/L) and 10 mg/L SO_3^{2-} , was prepared as follows: the sulphite stock solution was prepared by dissolving sodium sulphite salt in demineralised water; the Mn(II) stock solution was obtained by dissolving $\text{MnSO}_4 \cdot 4\text{H}_2\text{O}$ in demineralised water. The pH of the reaction mixture was 6.5 and it was aerated by the injection of fine bubbles of air.

After a 15 W low pressure mercury lamp was switched on to illuminate the reaction mixture for 2 minutes, the reaction mixture became cloudy because of the appearance of grey/black suspended particles indicating that an oxide of manganese had been formed. A 25 mL sample was collected and its pH (4 - 5) was adjusted to 7 using dilute sodium hydroxide solution in order to coagulate colloidal manganese oxide particles. After 30 minutes, to

allow the precipitated grey/black particles sufficient time to coagulate, the sample was filtered using an Amicon unit fitted with 0.025 μm membrane. The dissolved Mn concentration in the filtrate was 22 $\mu\text{g/L}$. This indicates
5 that most of the dissolved Mn(II) was oxidised to Mn(III)/Mn(IV) and precipitated as manganese oxide (which is black).

When the same procedures were repeated without illumination, the reaction mixture remained clear and
10 colourless. A sample was taken after 30 minutes and subjected to the coagulation and filtration procedure. The manganese concentration in the filtrate was 505ppb (Table 1).

Dissolved manganese concentrations were analysed
15 using ICP-MS, ICP-AES or atomic absorption spectroscopy with a graphite furnace.

The results of one SUCH procedure are summarised in Table 1.

20 Table 1

Residual manganese concentration in water after filtration.

Concentration in parts per billion

Initial Concentration	511 ppb
After 2 min illumination at pH 6.5 in the presence of 10 mg/L sulfite	22 ppb
After 30 minutes without illumination	505 ppb

25

Photo-Oxidation of Other Dissolved Compounds

The above procedures can also be employed with the photo-oxidation of dissolved compounds such as Se(IV), CN^- , Fe(II), Ni(II), V(IV), U(IV), and Ce(III). Oxidation
30 can be demonstrated by making up a reaction mixture containing an appropriate concentration of one or more of

these compounds. Dissolved sulphur species can be obtained from stock solution which can be prepared by dissolving either the equivalent sodium or calcium salt in water. The mixture can then be divided into three portions for a set of three tests:

1. No UV illumination. To the first portion of the reaction mixture, an appropriate amount of sulphite or sulphide is added from a concentrated stock solution. The mixture is aerated with a nitrogen-oxygen mixture of known oxygen partial pressure. Speciation of the oxidation state of the target substance and the sulphur at several time intervals was used to determine the reaction rate.
2. The second portion of the reaction mixture is aerated with the same oxygen/nitrogen gas mixture used in Test 1 and illuminated without the addition of a sulphur compound.
3. The final portion is aerated with the same addition of sulphite or sulphide as used in Test 1 and the light was then turned on to start the experiment. The oxidation rate is determined as above for As(III) and Mn(II).

25

Illumination can be achieved by placing a lamp either within an envelope inside the reaction vessel or such that the light radiates from above. Types of lamps used can include a high or low pressure mercury arc lamp, a Xenon arc lamp or a blacklight blue fluorescent tube.

It would be observed that the rate of oxidation of the target substance in Test 3 is greater than that in either Tests 1 or 2.

Procedure for Experiments Using Sulphur Dioxide Gas

The photo-oxidation reaction can proceed just as well when sulphur dioxide gas is used instead of sulphite salt.

In order to demonstrate this, for each target substance, a set of three tests can be performed as in the previous section. The reaction mixture can be sparged with a fine stream of gas bubbles. The partial pressure of oxygen, sulphur dioxide and nitrogen can be independently varied in the gas stream from 0 to 100%.

Test A Sulphur dioxide is added to the oxygen/nitrogen gas stream at a known partial pressure, in the absence of any illumination, and the rate of oxidation was determined by speciating the oxidation state of the target substance after several time intervals.

Test B The vessel is designed so that the second portion of the reaction mixture was illuminated with light from a lamp, in the absence of sulphur dioxide. The slow background oxidation rate (if any) is determined by speciating the target substance for oxidation state at several time intervals.

Test C The third portion of the reaction mixture is placed in the reaction vessel. Sulphur dioxide was added to the gas stream and the lamp is switched on at the same time, to mark the beginning of the experiment. The sulphur dioxide partial pressure is the same as that in Test A and the illumination source and lamp intensity were the same as that in Test B.

The rate of oxidation of the target substance in Test C would be greater than that in Tests A or B.

When the target substance is Mn(II), dissolved Mn is determined after filtration using a 0.025 μ m membrane filter as discussed above. Alternatively, electron paramagnetic resonance spectroscopy, can be used to determine dissolved Mn(II).

Whilst the invention has been described with reference to a number of preferred embodiments it should be appreciated that the invention can be embodied in many other forms.

CLAIMS:

1. A method for oxidising an inorganic species in an aqueous solution comprising the steps of:
 - (i) supplying an oxidisable source of sulphur, and
5 oxygen to the solution; and
 - (ii) irradiating the solution with UV light such that the species is oxidised.
2. A method as claimed in claim 1 wherein the oxidisable source of sulphur is SO_3^{2-} , S^{2-} , HS^- , $\text{SO}_2(\text{g})$,
10 aqueous SO_2 , HSO_3^- , $\text{S}_2\text{O}_3^{2-}$, $\text{S}_4\text{O}_6^{2-}$.
3. A method as claimed in claim 1 or claim 2 wherein the inorganic species is present in the aqueous solution in trace quantities.
4. A method as claimed in any one of the preceding
15 claims wherein the inorganic species is arsenic, cyanide, manganese, sulphide, selenium, vanadium, cerium, uranium, nickel and/or iron.
5. A method as claimed in any one of the preceding claims wherein the wavelength of UV light is less than
20 300nm.
6. A method as claimed in any one of the preceding claims wherein the UV light is provided in the form of sunlight.
7. A method as claimed in any one of the preceding
25 claims wherein dissolved oxygen is derived from air.
8. A method as claimed in any one of claims 1 to 6 wherein dissolved oxygen is derived from a gas source with an oxygen partial pressure of about 0.2 atmospheres.
9. A method as claimed in any one of the preceding
30 claims wherein the aqueous solution is one of: drinking water, industrial waste water, or an industrial process liquor.
10. A method for oxidising inorganic species in an aqueous solution substantially as herein described with
35 reference to the Examples.

DATED this 23rd day of July 1997

Australian Nuclear Science and Technology Organisation
and

5 CRC for Waste Management and Pollution Control Ltd

By their Patent Attorneys

GRIFFITH HACK

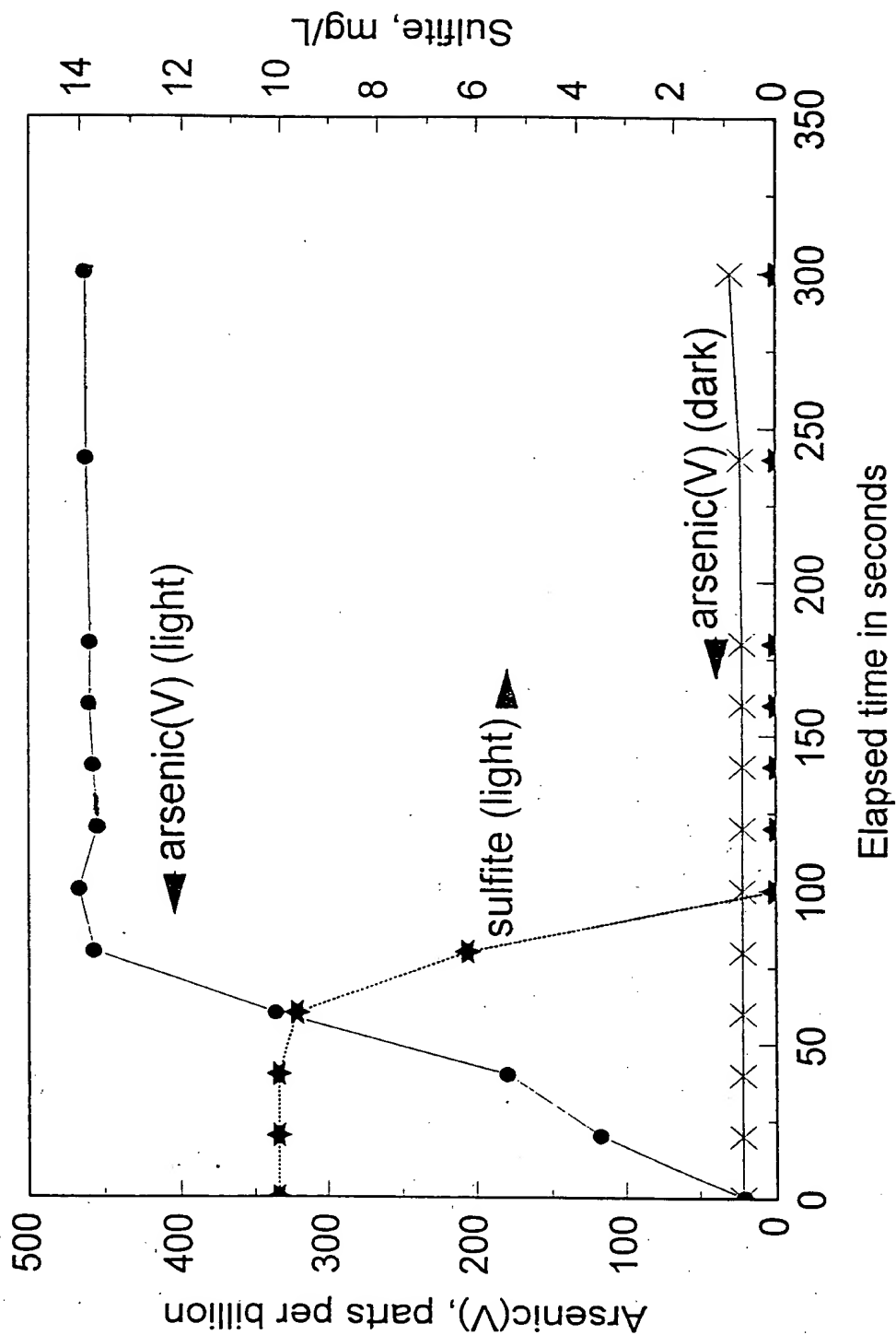


Figure 1

The increase in arsenic(V)-concentration and concomitant decrease in sulfite-concentration as a function of illumination time using a 15 W low-pressure mercury lamp. The corresponding change in arsenic(V) concentration in darkness is also shown. Initial conditions: 1.7 litre of solution containing 470 ppb arsenic(III) in the presence of 10 mg/L sulfite, solution pH adjusted to 9 using sodium carbonate.

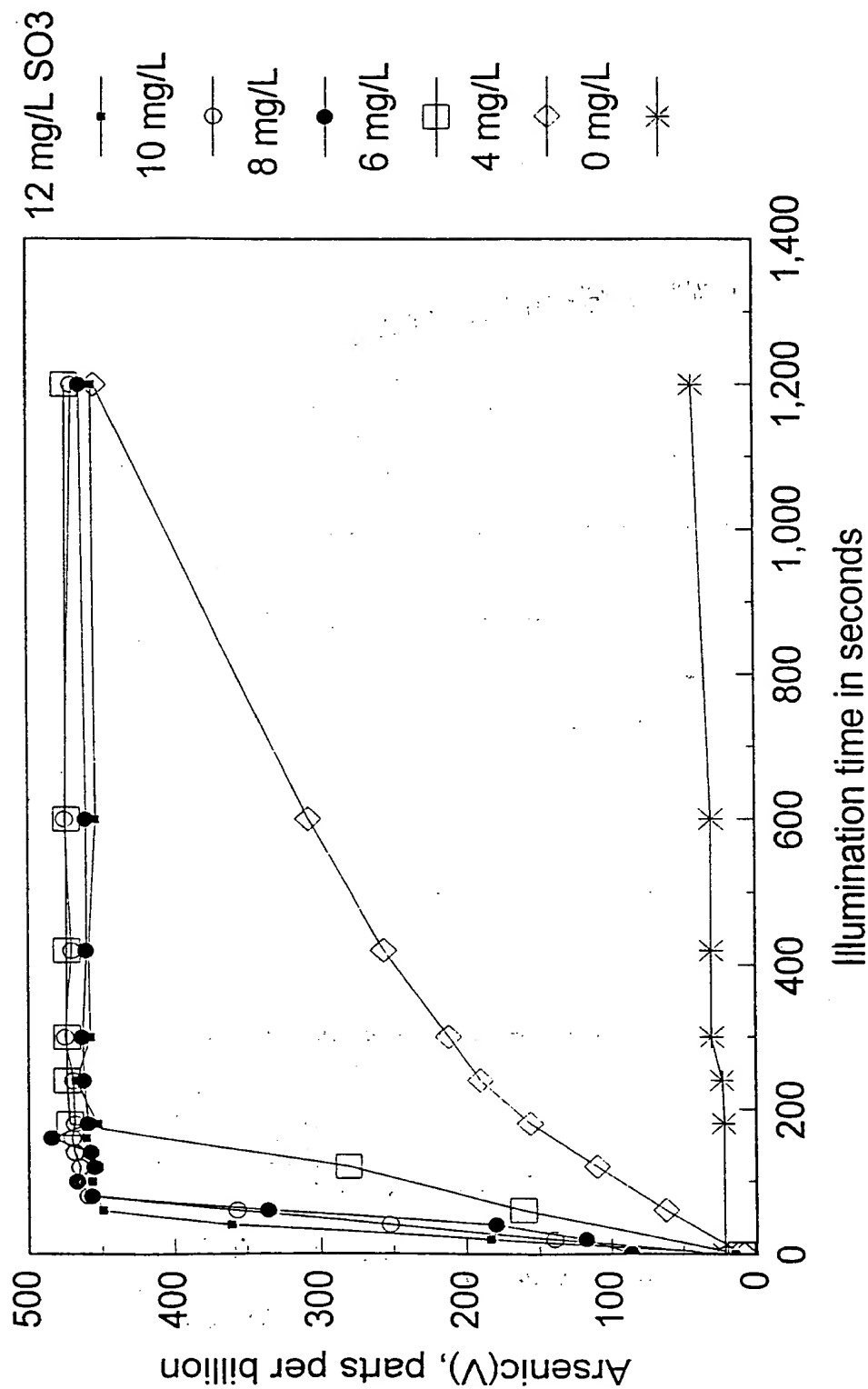


Figure 2

The increase in arsenic(V) concentrations as a function of illumination time using a 15 W 254 nm lamp. Initial conditions: 1.7 litre of solution containing arsenic(III) concentration of approximately 470 ppb, pH adjusted to 9 using sodium carbonate, initial sulfite concentrations varied from 0 to 12 mg/L.

THIS PAGE BLANK (USPTO)